

NASA Exobiology Program

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Annual Progress Report

Hydrocarbon biomarker stratigraphy of C-isotopic excursions marking chemical changes
in the ocean with contemporaneous biotic extinction-radiation events

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SCIENCE PROGRESS AND PLANS

Biomarker chemostratigraphy- identification of process-diagnostic hydrocarbons

One paper recording progress in this topic has been accepted for publication. We report a method for the rigorous identification of biomarkers (crocetane and PMI) that may be specific for methanotrophic and methanogenic archaea and, perhaps, the process of anaerobic oxidation of methane. If catastrophic methane efflux from sub-sea methane hydrate is responsible for extinction events, as has been hypothesized by many workers, then we might expect to find biomarkers for methane oxidation in sediments marking some extinction boundaries. Unfortunately, identifying crocetane and PMI with certainty is not a trivial exercise and these biomarkers appear to have been mis-identified in a recent publication by workers from Curtin University. Barber et al. (2001) identified crocetane and PMI in sediments deposited in the basal Triassic of the Perth Basin, Australia. However, Barber et al. (2001) also found crocetane and PMI in many other sediments and oils in a way that was inconsistent with our knowledge of these systems.

sediments and oils in a way that was inconsistent with our knowledge of these systems. Our study was, therefore, directed toward a more reliable protocol and correction of previous mistakes.

The paper is in press in Organic Geochemistry and the abstract is as follows:

GC-MS detection and significance of crocetane and pentamethylicosane in sediments and crude oils

by P.F. Greenwood and R.E. Summons

The occurrence of the archaeal biomarkers crocetane and pentamethylicosane (PMI) in sediments and crude oils was investigated using GC-MS and GC-MS-MS. Selected ion monitoring (SIM) and multiple reaction monitoring (MRM) protocols designed to detect the C₂₀ and C₂₅ irregular isoprenoids were evaluated. A method for the preferential detection of crocetane over phytane, its more abundant isomer, was refined using authentic compounds. Crocetane was found to be present in modern sediments from both aerobic and anaerobic water columns and in sediment from the 1640 Ma Barney Creek Formation providing evidence for the antiquity of its biosynthesis. Crocetane was also detected in several Perth Basin crude oils, in the Kockatea shale, their putative source rock and in Canning Basin oils, although MRM analysis could only verify its occurrence in Canning oils of Devonian age. Equivocal data from Ordovician and Carboniferous Canning Basin oils highlights the need for extreme caution when attempting to distinguish between acyclic isoprenoid isomers. PMI was identified by MRM in a Miocene Monterey sediment and in a modern Antarctica sediment. On the other hand, the C₂₅ isoprenoid hydrocarbon peak detected in Triassic and older sediments was consistently identified as the regular isomer (I_{25 reg}) whenever it was sufficiently abundant for MRM to be applied.

We are now embarking on a wider application of this methodology to observe how the absolute abundance of crocetane varies stratigraphically through later Permian and Early Triassic sections in the Perth Basin and the Meishan section of China.

Reorganisation of biogeochemical cycles

There are many hypotheses concerning the mechanisms of biotic extinction. Whatever the specific killing mechanism, extinction events are commonly marked by sharp excursions in the carbon isotopic composition of sedimentary carbonate carbon and sometimes in organic carbon. Mechanisms such as breakdown in productivity, overturn of a stagnant ocean and, again, catastrophic efflux and oxidation of methane have all been invoked to explain these excursions. Using a record of the isotopic compositions of marine C_{org} and C_{carb} through the last 800 Myr we re-assessed the common assumption that the carbon cycle operates in a steady state. We found steady state behavior in the Cenozoic and that the fractional burial of organic carbon is about 0.3, as is commonly believed. On the other hand, records of the Neoproterozoic suggested a fractional organic carbon burial ~ 1 during the intervals ca. 730-590 Ma and 580-555 Ma which is an impossible result. An alternative model of the oceanic carbon cycle was therefore devised. In it we considered two reactive carbon reservoirs namely dissolved and suspended organic carbon and dissolved inorganic carbon. These reservoirs were of vastly different sizes with the organic reservoir several orders of magnitude greater than today. Moreover, they cycled on different timescales. This model explains the Neoproterozoic isotopic records without appealing to unrealistic rates of remineralization of sedimentary reservoirs or massive amounts of hypothetical methane hydrates. Preliminary examination of isotopic trends during OAE's in the Mesozoic suggests similar mechanisms may operate. A paper reporting these observations, and inferences about animal evolution and the snowball Earth hypothesis has been accepted for publication in PNAS. The title and abstract is:

Dynamics of the Neoproterozoic carbon cycle

By Daniel H. Rothman, John M. Hayes and Roger E. Summons

The existence of unusually large fluctuations in the Neoproterozoic (1000--543--Ma) carbon-isotopic record implies strong perturbations to the Earth's carbon cycle. We analyze these fluctuations by representing them in a phase space defined by the isotopic content of carbonate carbon and the fractionation between carbonate and marine

organic carbon. We show that the resulting trajectories lie on an attractor whose quantitative features derive from the non-steady state dynamics of two reactive pools of carbon. The lack of a steady state is traced to an unusually large oceanic reservoir of organic carbon. We suggest that the most significant of the Neoproterozoic negative carbon-isotopic excursions resulted from increased remineralization of this reservoir. The terminal event, at the Proterozoic-Cambrian boundary, signals the reservoir's final diminution, a process which was likely initiated by evolutionary innovations that increased export of organic matter to the deep sea.

PERSONNEL

In the first year of this grant Dr Emmanuelle Grosjean was appointed as a postdoctoral fellow. Dr Grosjean recently completed her PhD at the Louis Pasteur University, Strasbourg and this is her first postdoctoral position. Since we were establishing a completely new program here at MIT, her initial aims were to help with equipment purchases, installation and to develop and verify laboratory protocols for hydrocarbon biomarker analysis. This was accomplished and we now have a smoothly functioning laboratory and standard operating procedures for a large range of analysis types. Dr Grosjean has also been training graduate and undergraduate students in these protocols. Dr Grosjean has since transferred to a petroleum industry-sponsored grant although she still works on issues that are central to our original NASA Exobiology proposal namely hydrocarbon biomarker chemostratigraphy in Neoproterozoic and Early Cambrian sediments of Oman.

In place of Dr Grosjean on this grant we have recently appointed Dr Gordon Love of the University of Newcastle Upon Tyne, UK. Dr Love, with 6 years postdoctoral experience, is a senior researcher in organic and biomarker geochemistry and an expert in analysis of kerogens by hydropyrolysis. He will use these techniques to examine the nature of Early Triassic marine organic matter (bitumens and kerogens) from the Perth Basin, Western Australia. We have also offered a short term (6 Mo) postdoctoral appointment to Dr Changqun Cao of the Nanjing Institute of Geology and Paleontology, Chinese Academy of Sciences. He has been measuring carbon isotopic excursions vs

rates of biotic extinction of Permian-Triassic boundary intervals in the Meishan area and has collected rocks from several new sections for biomarker analysis. Dr Cao's visit will provide him with training in organic geochemistry and will also help cement a collaborative relationship with the Chinese scientists who are studying the best documented of the P/T boundary events. Both Dr Love and Dr Cao will join our MIT lab in August 2003.

Ms Carolyn Colonero has joined our laboratory as mass spectroscopist and laboratory manager and is partly supported on the Exobiology grant. Prior to coming to MIT Ms Colonero worked in industry as an isotope mass spectroscopist and brings important skills to this project. Louisa Bradtmiller, a recent graduate in geology has also been partially supported as a technical assistant.

EQUIPMENT AND LABORATORY FACILITIES

A very large proportion of the Exobiology grant to MIT comprised funds to purchase a GC-MS-MS system and thereby develop a state-of-the-art organic mass spectrometry facility here. The PI and a colleague, Dr Jochen Brocks of Harvard University, spent several weeks in late 2002 evaluating prospective mass spectrometers and their manufacturers to determine the most suitable instrument for our purposes. Our decisions were made difficult by the fact that the main market for high resolution GC-MS-MS systems is in dioxin analysis. Proteomics is the main use of high resolution LC-MS-MS systems. Consequently, hardware configurations and software developments necessary for high-end biomarker analysis lagged behind these other applications. In the final analysis, the Micromass Autospec GC-MS-MS system (marketed by Waters Corporation) was the only instrument that fulfilled our specific requirements. We ordered an Autospec Ultima GC-MS with an additional quadrupole mass analyzer system in December 2002. The main GC-MS system was delivered at the beginning of April and the Q analyzer will be retrofitted in May. When the installation is complete in May-June 2003 we will have a fully capable GC-MS-MS system. A graduate student, Jennifer Eigenbrode who is

affiliated with the Penn State NAI node will be the first visitor to use the system for analyses of Archean hydrocarbon samples.

SUMMARY

We have made significant progress in setting up the geochemistry laboratory at MIT for high sensitivity, high resolution biomarker analysis. This includes establishing laboratory protocols and purchase and installation of state-of-the-art equipment. We have also continued to progress our science objectives with a new hypothesis about the causes of large carbon isotope excursions in the Neoproterozoic and expect that the resultant publication will attract considerable interest (and possibly controversy). We have developed a new analysis scheme to detect hydrocarbons that are associated with anaerobic oxidation of methane and will use it to explore boundary events for evidence of enhanced methane oxidation. Two new postdoctoral fellows will join the group in the next few months to work on P-T boundary sections from Australia and China.